Product Stewardship Considerations in the Use of Polyacrylamides in Soil Erosion Applications

by R. Deskin, Ph.D., DABT, Cytec Industries Inc.

Product Stewardship is a global term which arises from Responsible Care initiatives originating in the United States, Canada and Europe. Product Stewardship is an extension of previously existing product safety programs, the principles of which are applied to all aspects of the product life cycle. Where product safety was concerned only with the product in its package, Product Stewardship addresses the product, its manufacturing process and applications. Hence, we look at the product, how it is made, how it is used and how its residual is disposed of. The essence of Product Stewardship is the responsible and ethical management of our products from design to ultimate disposition or from cradle to grave. The cornerstone of Product Stewardship is the Product Life Cycle. The life cycle is meant to be continuous and includes customer need, raw materials acquisition, product design and development, manufacturing, product distribution, product usage, recycle and reuse and disposal. As the life cycle is viewed in a continuum, entry into the cycle can begin at any point. Usually, customer need drives the life cycle for new products. Changing and evolving regulations can triggered product re-design/refinement.

A comprehensive product safety program has been in existence at Cyanamid/Cytec since the early 1950s. Hazard class-ification was at the core of the program. In evaluating the risk of a product, one takes into account hazard and exposure, as hazard and exposure comprise risk. Hazard is a materials intrinsic potential to cause harm. This may include health, physical or environmental effects. Exposure is the contact that a material makes with human, animal or plant life, or with air, water or soil. Risk is the combination of hazard and exposure that establishes the probability of an occurrence of an unwanted adverse effect on human health or the environment. Risk management, on the other hand, is the proactive effort to reduce potential risk, either through reducing the hazard, reducing exposure or reducing both. Reducing the hazard, which is an intrinsic characteristic of the material, usually requires product reformulation. That is, the substitution of a raw material for a less toxic raw material or process changes which reduce residual levels of potentially hazardous materials. Safety, on the other hand, is the relative protection from adverse consequences. That is, the absence of risk.

A program to assess risk starts with an assessment of hazard. As we said, hazard includes physical, health and environmental hazard. Physical hazard is an intrinsic property of a material which can only be modified by changing chemical formulation or modifying the manufacturing process. Physical hazards can include flammability, combustibility, reactivity, explosivity or slippery spills (e.g. PAM's), etc. These hazards can be reduced by solvent replacement for example. Replacement of isopropanol with propylene glycol or isobutanol can significantly alter flash point to make a flammable material no longer such. This is addressed by the design/development and raw materials acquisition phase of the product life cycle.

Health hazards are assessed by conducting a battery of toxicology evaluations. This includes an assessment of acute effects (i.e. effects that result from a single exposure) or chronic effects (i.e. effects resulting from long-term repeated exposure). Acute effects are associated with lethality or death. This includes an assessment of LD (lethal dose) of LC (lethal concentration) in laboratory animals. Here the endpoint is the dose or concentration of a material which results in 50% mortality within a given period of time. Oral, inhalation and dermal are the most common routes of exposure. The lower the LD/LC 50 number, the greater the toxicity. An oral LD50 of 50 mg/kg or less would be considered very toxic. Irritation is soreness, redness, roughness or inflammation of bodily tissues. It can range from reversible mild/moderate effects to irreversible chemical burns. Organic solvents for example produce a mild/moderate skin or eye irritation, while sulfuric acid or sodium hydroxide produce a serve chemical burn.

Sensitization, also considered an acute effect, is an allergic reaction resulting from repeated exposure to a chemical. A common example of sensitization is exposure to poison ivy. Chemical induced allergy can be induced by epoxy resins (skin contact) or isocyanates (inhalation exposure). With sensitization, an initial exposure period not resulting in an effect is needed for antigen/antibody buildup. Subsequent exposures trigger the adverse effect. Chronic effects include birth defects, reproductive disorders, cancer and organ system damage. Birth defects are deleterious structural malformation in a fetus. Ethanol and organic mercury commonly produce birth defects in laboratory animals and may produce this same in man. Adverse effects of chemicals that interfere with the ability of males or females to reproduce are classified as reproductive toxins. Toluene and acrylonitrile cause such effects in animals.

Cancer is defined as the uncontrolled cell death resulting in the formation of tumors. Evidence of carcinogenicity comes from human epidemiology studies or chronic animal toxicity studies. acrylamide monomer, formaldehyde and acrylonitrile have been shown to cause cancer in laboratory animals. Human epidemi-

ology studies indicate that there is no evidence that acrylamide causes cancer in humans. Chemicals may present immediate or delayed hazards to human organs or systems. The site of the adverse effect may be distant from the initial contact point of the chemical. Ethanol, for example, causes liver effects following oral ingestion.

The impact of chemicals on the environment is assessed by using aquatic and environmental endpoints. Aquatic toxicity is assessed as the lethality to fish and aquatic organisms. The LC50 (lethal concentration required to kill 50% of the organisms in a given time) is the common measure. The lower the LC50, the greater the toxicity. Nonyl phenol, for example, has an LC50 of less than 1 ppm (mg/l), making it highly toxic. Bioaccumulation is defined as the concentration build-up of a material over time. The octanol/water partition coefficient is a measure of Bioaccumulation potential. The lower the octanol/water partition coefficient, the more water soluble a material is. Acrylamide, for example, has a log Kow of 0.31, indicating it to be highly water soluble. Organic mercury is another material that builds-up over time. Minamata Disease in Japan resulted from organic mercury waste being dumped in to the ocean and bioaccumulation in fish. Persons eating the fish suffered from neurological and reproductive effects of organic mercury. Biodegradability is the rate and degree of chemical breakdown in soil or water. BOD and COD are indicators of a material's biodegradability potential.

Persistence is the ability of a material to exist in the environment without changing. The half-life of a chemical in soil or water is an indicator of persistence. The larger or longer the half-life, the greater the persistence. The pesticide DDT and polychlorinated biphenyls (PCBs) have been shown to be persistent in the environment. With the passage of the 1990 Clean Air Act amendments, there have been increasing scrutiny on materials which have the potential to damage the ozone layer. This includes the concentration of VOC's in a product and their ability to be released during usage.

Once an assessment of physical, health and environmental hazards of a material are made, one needs to evaluate potential for exposure. One way of minimizing risk is to minimize or eliminate exposure. With regard to exposure, we include, duration/frequency of exposure, route of exposure and concentration/degree of exposure. Exposure control measures can include engineering controls and/or the use of personal protective equipment.

The principle of Product Stewardship, outlined above, have been applied to the use of polyacrylamide in soil erosion applications. Results of hazard assessment indicate that the polymer itself is non-toxic. This owes itself to its high molecular weight (7-15 million g mol^{-1} which is not readily absorbed by the gastrointestinal tract. Polyacrylamides can be positive, negative or neutral in charge. The molecular weight of PAMs commercially available range from a few thousand to 20 million.

Polyacrylamides exhibit a low order of toxicity to mammalian systems, including high acute oral LD50 values by the oral and dermal routes (> 5 grams/kg). Slight dermal and eye irritation have been noted at high doses. No significant adverse effects were seen in chronic oral studies in rats and no compound-related reproductive effects were seen in a three-generation study in rats. Human epidemiology studies demonstrated no association between unintentional occupational exposure to PAMs and tumors. Emulsion PAMs produce slight to severe skin and eye irritation.

The toxicity of acrylamide monomer (AMD) has been well characterized. Acrylamide was acutely toxic to rats when given orally and to rabbits when applied dermally (LD50 values of 295 mg/kg and 252 mg/kg, respectively). AMD caused moderate skin and eye irritation in laboratory animals. AMD is a well-known neurotoxicant. It produces a distal-to-proximal dying back axononopathy in the peripheral nervous system. Initially, portions of the large diameter nerve fibers in the extremities are affected. With prolonged exposure, the fiber degeneration processes up the arms and legs affecting regions closer to the brain. The functional indicators of AMD toxicity include both sensory loss and motor weakness. Regeneration of affected nerves takes place after cessation of exposure.

Acrylamide has been tested for mutagenicity in a battery of genetic toxicology tests. Acrylamide does not induce point mutations. Acrylamide has been shown to be inactive in the Ames test. Similarly, AMD did not increase the frequency of sister-chromatid exchanges in CHO cells in tissue culture. AMD did not induce a positive response in the CHO/HGPRT forward mutation assay. In contrast to the studies listed above which test for direct interactions with DNA, studies which evaluate the effects on chromosomes indicate that AMD can break chromosomes in rats and mice. AMD has been shown to induce dominant lethals in rats and heritable translocations in mice, both at doses which cause neurotoxicity. It has been shown that AMD reacts preferentially with the proteins of the chromosomes rather than directly with DNA. The weight of the evidence indicates that AMD does not react directly with chromosomes.

An initial lifetime study in rats where acrylamide was administer in the drinking water indicated that a variety of tumors could be produced by AMD at doses of 2 mg/kg/day. A second lifetime study was conducted by Cytec to clarify the results seen from the first study. In this study, male F344 rats received 0.1, 0.5, and 2 mg/kg/day and female F344 rats received 1 and 3 mg/kg/day in their drinking water for 2 years. The only malignant tumor significantly increased in this study was testicular mesothelioma observed in the 2 mg/kg dose group only. Testicular mesothelioma is a tumor site unique to male rats. Non-malignant tumors of the thyroid were increased at doses above 0.5 mg/kg. Mammary tumors were statistically increased but were in the historical control range.

Two epidemiology studies have been completed on workers exposed to acrylamide. In the first study, although no excess cancer mortality was noted when the mortality patterns of 371 employees exposed to AMD were examined, the limited sample size precluded a valid assessment of the carcinogenic potential to man. In

a second study, mortality from all causes among 2293 acrylamide exposed workers was 11% less than expected based on comparison with the US general population. These more recent epidemiological study results indicate that occupational exposure to acrylamide was not associated with a statistical increase in cancer.

The environmental effects of polyelectrolytes has been addressed as well. Cationic polymers have been shown to be toxic to fish when evaluated in pristine water in the absence of suspended solids. Addition of humic acid as a source of suspended solids reduces the toxicity of cationic polymers as evidenced by an increase in LC50 values. Mechanistic studies reveal that cationic polymers, in the absence of suspended solids, bind to fish gills and produce a mechanical suffocation as opposed to systemic toxicity. Anionic PAMs show a reduced aquatic toxicity profile. In addition, they do not cause adverse effects on plants, worms, soil nutrients or nitrifying bacteria. Additional environmental considerations with regard to emulsion polyacrylamides include oils and surfactants. Nonyl phenol, for example, has been shown to be fairly toxic to fish (LC50 < 1 ppm). Degradation of PAMs in soil is anticipated to occur with time as a result of mechanical degradation, chemical and biological hydrolysis, sunlight, salt and temperature effects. Polymer degradation has been reported in the literature to be approximately 10% per year. PAM degradation does not release free acrylamide monomer. Polyacrylamide products are currently manufactured to specifications which reduce residual AMD monomer content to < 0.05% residual AMD. Fate and effect studies reveal that AMD is not taken up into plants. This has been demonstrated in tomatoes, corn and beans.

Table 1

Species	LC50 (ppm)	Duration of Test
Bluegill Sunfish	100	96 hr.
Rainbow Trout	110	96 hr.
Fathead Minnow	120	96 hr.
Daphnia Magna	160	48 hr.
Midge Larvae	410	48 hr.

The aquatic toxicity of acrylamide monomer has been determined in flow-through studies. The results indicate that the monomer is non-toxic to aquatic organisms. See table 1.

Acrylamide monomer is biodegradable in the environment. The BOD5 is 54 to 75% of theoretical and the BOD20 is 100% of theoretical.

Conclusion

Product Stewardship is the ethical and responsible management of products from design to ultimate disposal. As an extension of Product Safety, we are no longer limited in scope to just evaluating the product in its package. Product Stewardship looks at design/development, manufacture, packaging, disposal, energy conservation, raw materials, transport and ultimate disposal. It is full environmental cost accounting applied to products. At the cornerstone of Product Stewardship is the product Life Cycle. One must consider all aspects of the product Life Cycle. As a component of the Life Cycle is manufacture, use and disposal of products. An evaluation of product applications is part of the process. For polyacrylamides, the data supports the use of these products in soil erosion applications. The polymers are non-toxic and not harmful to the environment. The monomer level has been greatly reduced over the years. AMD monomer, while neurotoxic to man and animals) and carcinogenic in animals is readily water soluble and biodegrades rapidly in the environment. Polymer does not biodegrade to monomer in the environment. There is no indication of any adverse impact on soil systems and plants when anionic PAMs are used in soil erosion application.